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Stability, Reactivity, Selectivity, Catalysis, and Predictions of 1,3,2,5-Diazadiborinine: Computational Insight into a Boron−Boron Frustrated Lewis Pair

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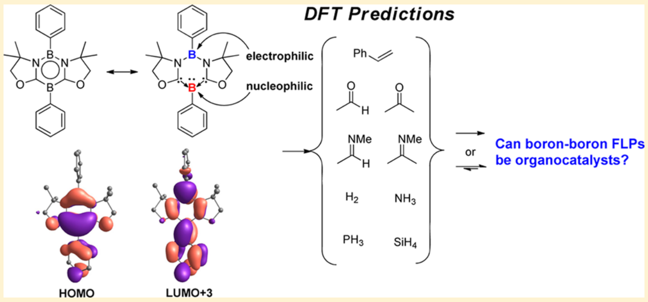
S *Supporting Information*

ABSTRACT: Recent progress in frustrated Lewis pairs (FLPs) has attracted increasing attention. However, most of the FLPs are composed of Lewis basic phosphines and Lewis acidic boranes. In 2015, Kinjo and co-workers reported the first intramolecular boron−boron FLP, namely, 1,3,2,5-diazadiborinine (**1**), which showed high regioselectivity in the reactions with methyl trifluoromethansulfonate, phenylacetylene, and CO_2. More interestingly, the activation of CO_2 was found to be reversible when the temperature was elevated to 90 °C. Here, we performed thorough density functional theory (DFT) calculations to understand the stability, reactivity, and selectivity of **1**. The electronic effects and favorable orbital overlap of **1** with substrates play a crucial role in the reactivity and regioselectivity. On the basis of the results, several organic substrates activated by **1**, including aldehyde, ketone, imine, hydrogen, ammonia, phosphine, and silane, were explored computationally. The results show that the combination of aldehyde, ketone, imine, and silane are reversible, especially at elevated temperatures. Finally, we modeled the hydrophosphination of Me_2PH and phenylacetylene catalyzed by **1**. The rate-determining step is the hydrophosphination with an activation barrier of 31.7 kcal/mol, indicating that the process might be possible. Our results may open an avenue to design new organocatalysts.



INTRODUCTION

Since the pioneering work of the reversible hydrogen activation by Stephan in 2006,[1] research progress on frustrated Lewis pairs (FLPs) has achieved tremendous success for their ability to activate small molecules and act as metal-free catalysts.[2] In most of the FLP systems, phosphines and boranes, in which the phosphorus and boron adopt the +III oxidation state, containing a lone pair of electrons and an empty orbital, act as Lewis base and Lewis acid, respectively.

Recently, the groups of Bertrand[3] and Kinjo[4] independently developed neutral tricoordinate organoboron species, featuring a +I oxidation state boron center, which behave as electron pair donors, or Lewis bases (Figure 1a). These nucleophilic organoboron compounds are isoelectronic with amines and phosphines and could be readily protonated by trifluoromethanesulfonic acid[3,4a] or even coordinated to transition metals.[4] These results posed an interesting question as to whether boron−boron FLPs are possibly achievable. Indeed, very recently, an aromatic 1,3,2,5-diazadiborinine (**1**) (Figure 1b),[5] featuring both nucleophilic and electrophilic boron centers, was prepared by Kinjo and co-workers. Compound **1** can be formally considered as a B(+I)/B(+III) donor−acceptor system, which is thermally stable (mp 133 °C without decomposition) and displays FLP-type reactivity when exposed to phenylacetylene and CO_2 (Figure 1b). Interestingly, the activation of CO_2 by **1** was found to be reversible, foreshadowing a potentially useful application of boron−boron FLPs in organocatalysis.

Inspired by the intriguing results, here we report thorough density functional theory (DFT) calculations to investigate in detail the stability, reactivity, and selectivity of 1,3,2,5-diazadiborinine (**1**). Furthermore, a computational prediction was carried out to probe the small molecule (aldehyde, ketone, imine, hydrogen, ammonia, phosphine and silane) activation ability of **1**. Our findings may provide hints for further developments of new boron−boron FLPs and their applications in catalysis.

COMPUTATIONAL DETAILS

Calculations were carried out with the Gaussian 09 package.[6] Geometry optimizations were performed with the B3LYP functional.[7] The 6-31G(d)[8] basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of

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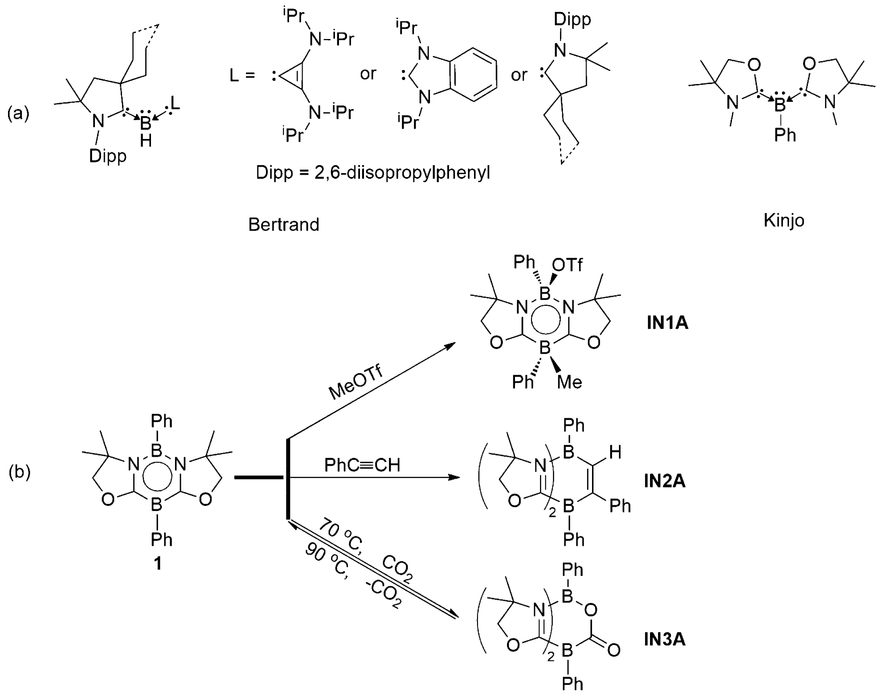

Figure 1. (a) Neutral nucleophilic tricoordinate organoboron species reported by Bertrand[3] and Kinjo,[4] respectively. (b) 1,3,2,5-Diazadiborinine (**1**) and its preliminary reactivity.

imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy and highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs). Dispersion correction calculations using the corresponding B3LYP-D functional were performed with the DFT-D3 program of Grimme.[9] Transition states were submitted to intrinsic reaction coordinate (IRC)[10] calculations to determine two corresponding minima.

The M06-2X functional[11] was used for solution-phase, single-point energy calculations because this method was recently established as an excellent functional for describing reaction energetics of main group systems.[12] The gas-phase geometry was used for all the solution phase calculations. A similar treatment was also used in many recent computational studies.[13] A larger basis set, that is, 6-311++G(2d,p),[14] was used. The default self-consistent reaction field (SCRF) polarizable continuum model (PCM) was used with acetonitrile (for the reaction of **1** with MeOTf only) and benzene, while Bondi radii[15] were chosen as the atomic radii to define the molecular cavity. The Gibbs energy corrections from frequency calculations and dispersion corrections were added to the single-point energies to obtain the Gibbs free energies in solution. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298 K. Natural bond orbital (NBO) calculations were carried out using the NBO 5.9 program[16] at M06-2*X*/6-311++G(2d,p)//B3LYP/6-31G(d) level. Optimized structures were visualized by the CYLview program[17] or Chemcraft.[18]

■ RESULTS AND DISCUSSION

For a better understanding of the bonding situation and stability of **1**, natural bond orbital (NBO) calculations were performed at the M06-2*X*/6-311++G(2d,p)//B3LYP/6-31G(d) level of theory (Figure 2). Figure 2a depicts the selected NBO and Mulliken charges and Wiberg bond indices (WBI) of **1**. The NBO and Mulliken charges of B1 are 0.96 and 0.14 au, which are much more positively charged than those of B4 (0.17 and −0.31 au), suggesting that B1 is much less nucleophilic and more electrophilic than B4. The WBI analysis shows that both N2−C3 (1.14) and C3−B4 (1.22) have partial double bond characters.

Furthermore, the optimized structure of **1** (Figure 2b) shows that B4 is in a planar environment (sum of the angles: 360°) and C3−B4 bond length (1.496 Å) is shorter than the Pyykkö/Atsumi standard value[19] for C−B (1.600 Å), which is consistent with the studies of borylene complexes $(BH)L_2$ (L = Lewis bases) by Frenking.[20] This could be an indication for the back-donation of the p(π) lone-pair orbtial of B4 into the formally vacant p(π) AOs of the bonded carbons. As discussed above, coupled with the FLP-type reactivity of **1**, suggested the electronic structure is best described by a B(I)/B(III) mixed-valence six-membered ring (Figure 2c). The very weak interaction between the vacant orbital of B1 and the lone pair of B4, the nature of the FLPs, is indicated by the small WBI (0.07) of B1 and B4 (Figure 2a).

Kinjo and co-workers demonstrated the six-membered $B_2N_2C_2$ ring is aromatic, featuring delocalized π bonds over the ring plane.[5] In fact, not only are the π bonds delocalized over the central ring, but also from the lone pairs of the oxygen atoms. Selected natural localized molecular orbitals (NLMOs) are illustrated in Figure 2d, displaying the highly delocalized π bond contributions from the oxygen atoms, which can further stabilize the electron-deficient boron centers. Indeed, the second-order perturbation theory of the NBO method shows a strong hyperconjugative delocalization from the p-type O5 lone pair to the polar N2−C3 π^* antibond with a donor−acceptor stabilization energy of 43.2 kcal/mol (Figure 2e). Similarly, the powerful π-type conjugative delocalization from the N2−C3 π bond to the B1 and B4 lone pair antibonding orbitals provides 37.9 and 7.8 kcal/mol stabilization energies, respectively.

Importantly, the reactions between **1** and different organic substrates proceed with high regioselectivity, and the activation of CO_2 was found to be reversible (Figure 1b). For example, methyl trifluoromethansulfonate (MeOTf) was added into an acetonitrile solution of **1** and stirred for 1 h at room temperature. After workup, colorless compound **IN1A** was isolated in 75% yield as the only product. To gain more insight into the high reactivity and regioselectivity, we performed the mechanism study at the SCRF-

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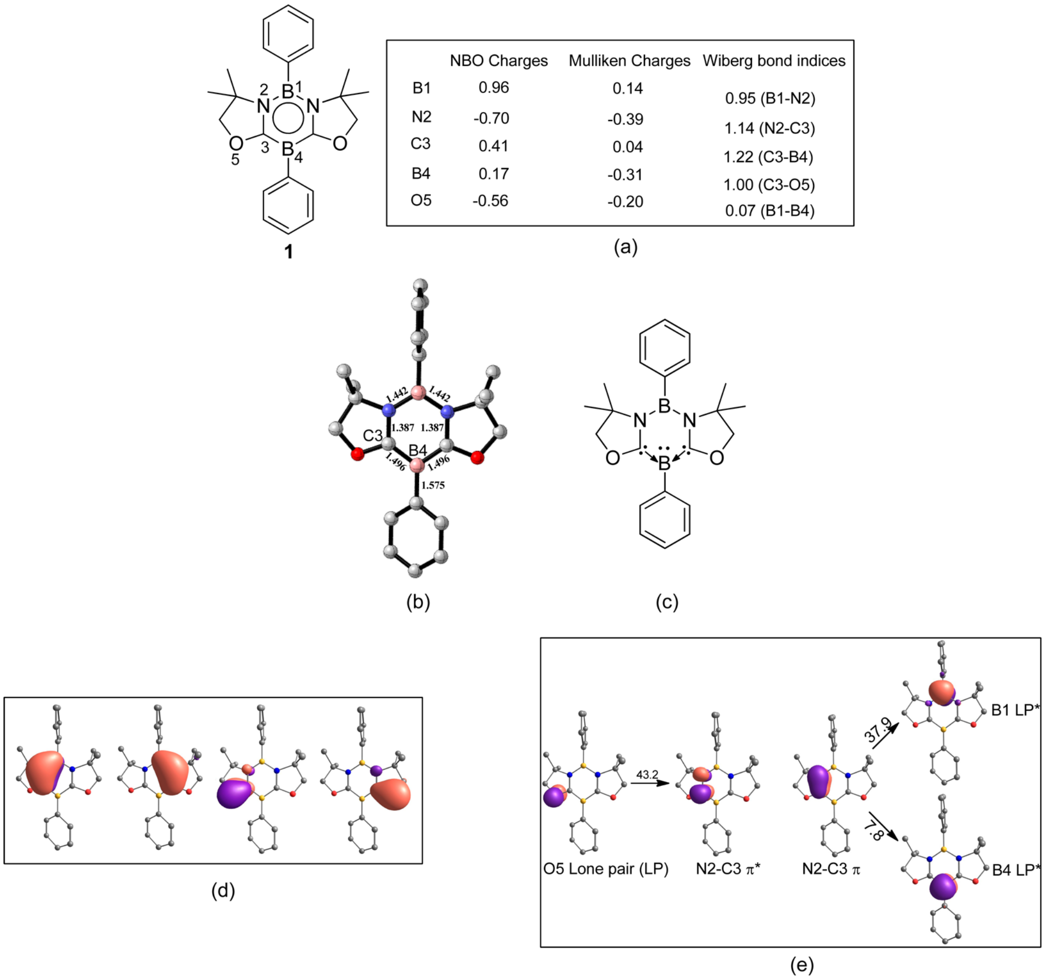


	NBO Charges	Mulliken Charges	Wiberg bond indices
B1	0.96	0.14	0.95 (B1-N2)
N2	-0.70	-0.39	1.14 (N2-C3)
C3	0.41	0.04	1.22 (C3-B4)
B4	0.17	-0.31	1.00 (C3-O5)
O5	-0.56	-0.20	0.07 (B1-B4)

Figure 2. (a) Selected NBO and Mulliken charges and WBIs. (b) Optimized structure of **1** (bond lengths are given in Å). (c) Electronic structure of **1**. (d) Selected NLMOs of **1**. (e) Selected NBOs for the second-order perturbation theory analysis (energies are given in kcal/mol).

M06-2*X*/6-311++G(2d,p)//B3LYP-D/6-31G(d) level of theory (Figure 3a). We first modeled the reaction of **1** with MeOTf. The transition states **TS1A** and **TS1B** were located with the B4 and B1 centers of **1** attacking the methyl group of MeOTf, respectively. As expected, the free energy of **TS1A** (30.5 kcal/mol) is much lower than that of **TS1B** (49.6 kcal/mol), which could be mainly attributed to the electronic effects and frontier molecular orbital interactions (Figure 3b). As discussed above, B4 is much more nucleophilic than B1. The orbital coefficients (Figure 3b, in blue) of B1 and B4 of HOMO are 0.20 and 0.27, respectively, whereas those (in red) of LUMO+3 are 0.37 and 0.19, clearly showing that attacking electrophiles by B4 and accepting electrons from nucleophiles by B1 leads to the favorable orbital overlap. Moreover, **TS1A** leads to the more stable product **IN1A** (−60.2 kcal/mol), indicating path 1A is favorable both kinetically and thermodynamically, which is in excellent agreement with the experimental observations.

We next turned our attention to the unsymmetrical alkyne phenylacetylene and CO_2. Not surprisingly, the regioselectivity was determined by the nature of electronic properties of the substrates as illustrated in Figure 3. For example, it is much easier for B4 to attack C6 (Figure 3b, NBO charges: −0.04 au) over C7 (−0.19 au) of phenylacetylene. The activation energy is 5.8 kcal/mol, which is significantly lower than that of attacking C7 (10.4 kcal/mol). Our results show that both **IN1A** (−60.2 kcal/mol) and **IN2A** (−30.6 kcal/mol) are quite stable, and the reactions of **1** with MeOTf and phenylacetylene are irreversible. However, experimentally, the CO_2 activation by **1** was found to be reversible (Figure 1b). Treatment of **IN3A** at 90 °C for 50 min quantitatively regenerated **1**. As expected, the activation energy is only 24.2 kcal/mol from **IN3A** (−11.7 kcal/mol) to the corresponding transition state **TS3A**. On the basis of our findings above, the electronic effects play a key role in the reactions. The favorable reactive sites lead to the lower barrier process. Note that the reaction of **1** with MeOTf occurs at the room temperature. However, the computed energy barrier for path 1A is much higher than those of paths 2A and 3A (Figure 3a), which is inconsistent with the experimental observations. We argued that MeOTf might be preactivated by the very polar solvent acetonitrile, which could weaken the C−O bond in MeOTf.

Recently, main group compounds acting as metal-free catalysts have attracted considerable attention,[21] especially the FLP systems.[2] Encouraged by many achievements in theoretical predictions,[20,22] we computationally investigated the ability of **1** to activate several unsaturated organic substrates, including styrene, acetaldehyde, acetone, *N*-ethylidenemethanamine, and *N*-(propan-2-ylidene)methanamine (Table 1). Surprisingly, the activation barriers (less than 3 kcal/mol) are quite low for all the transformations. There are strong interactions between the HOMOs of **1** and LUMOs of the unsaturated substrates in the transition states (see the Supporting Information for details). The reverse processes (1S → **1** + S, entries 1−5) are easy enough

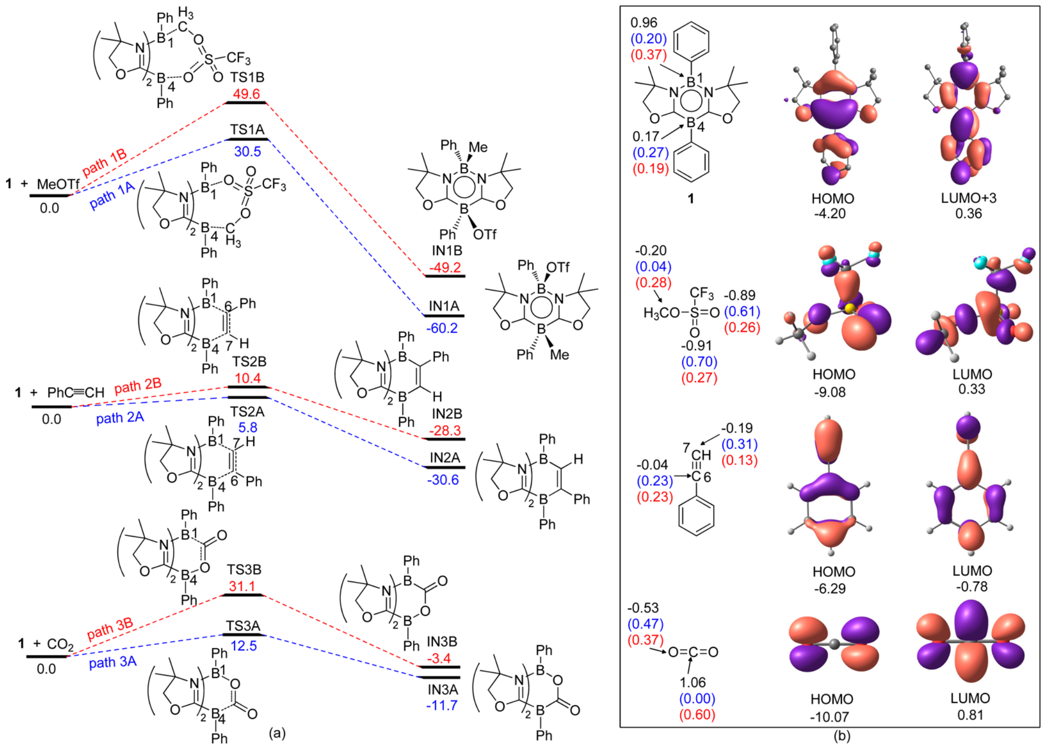
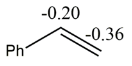
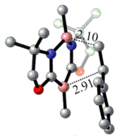
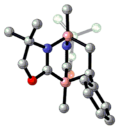
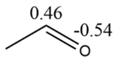
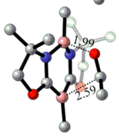
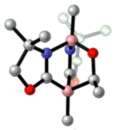
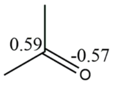
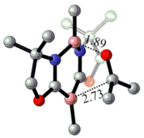
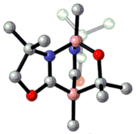
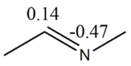
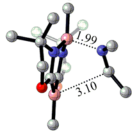
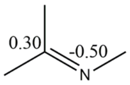
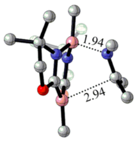
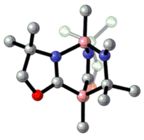


Figure 3. (a) Mechanism study of **1** with MeOTf, phenylacetylene, and CO_2 (energies are given in kcal/mol). (b) Selected NBO charges (in black) and orbital coefficients of HOMOs (in blue) and LUMOs (in red). Selected frontier molecular orbitals (energies are given in eV).

Table 1. Activation of Unsaturated Organic Substrates[a]

$$\underset{(0.0)}{\mathbf{1} + \mathrm{S}} \rightleftharpoons \underset{\mathrm{TS}}{[\mathbf{1}\cdots\mathrm{S}]^{\neq}} \rightleftharpoons \mathbf{1S}$$

Entry	S	3D Structures of TS	ΔG_{TS}	3D Structures of 1S	ΔG_{1S}
1			2.3		-21.9
2			0.1		-26.5
3			1.3		-23.4
4			2.2		-14.2
5			2.0		-16.2

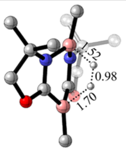
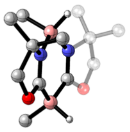
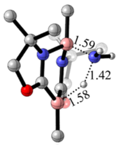
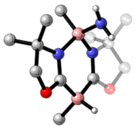
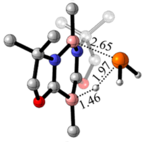
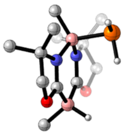
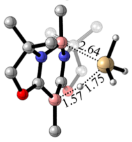
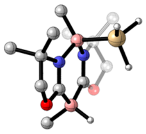
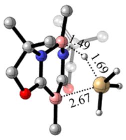
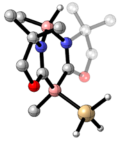
[a] Energies are given in kcal/mol. Bond lengths are given in angsroms. Selected NBO charges are given in atomic units. The phenyl groups on the boron centers and the hydrogen atoms attached to carbons are omitted for clarity.

to occur relative to the CO_2 process (reverse barrier is 24.2 kcal/mol), especially at elevated temperature. For example, the transition state (TS) for the styrene activation does not appear to be energy demanding (Table 1, entry 1). Also, the free energy of the product is only 24.2 kcal/mol lower than that of the TS. The combination of **1** with aldehyde (entry 2) and ketone (entry 3) is much stronger than those of imines (entries 4 and 5), based on the free energies of the corresponding **1S**, which might be mainly attributed to the more polar C=O π bond than that in C=N.

Small molecule activation has long been known for transition metals.[23] Recent progress in main group compounds activating small inorganic molecules has been independently reported by the groups of Power,[24] Stephan,[1,25] Bertrand,[26] and Kinjo.[27] Here, we evaluate the ability of **1** to activate H−H, H−N, H−P, and H−Si bonds (Table 2). For both transition metals and main group compounds, the combination of filled orbitals donating electron density into the σ*-orbital of H−X (X= H, N, P, and Si) and empty orbitals accepting electron density from the H−X σ-bond enables H−X bond cleavage. Indeed, the HOMOs of the transition states for H−X bond cleavage showed strong interaction betweens the HOMO of **1** and the LUMOs of H−X (see the Supporting Information for details). The activation energies for the H-–X (X = H, N, and P) bond cleavage are computed to be 28.2, 20.3, and 25.5 kcal/mol, respectively, indicating that these processes could occur at high temperature. However, the H_2 activation is highly exergonic with an energy of −37.9 kcal/mol, whereas the NH_3 (−13.4 kcal/mol) and PH_3 (−6.7 kcal/mol) activations are less exergonic. Since the H atom in SiH_4 has a marked hydridic character, the formation of the B1−H and B4−Si bonds is expected. Two regioisomers for the activation of SiH_4 were investigated (Table 2, entries 4 and 5), showing that B4 attacking Si of SiH_4 is much easier (14.4 kcal/mol) compared to attacking H (26.0 kcal/mol). The activation of

Table 2. Activation of Inorganic Small Molecules[a]

$$\underset{(0.0)}{\mathbf{1} + \mathrm{HX}} \longrightarrow \underset{\mathrm{TS}}{[\mathbf{1}\text{----}\mathrm{HX}]^{\neq}} \longrightarrow \mathbf{1HX}$$

Entry	HX	3D Structures of TS	ΔG_{TS}	3D Structures of 1HX	ΔG_{1HX}
1	H_2		28.2		-37.9
2	NH_3		20.3		-13.4
3	PH_3		25.5		-6.7
4	SiH_4		26.0		-0.9
5	SiH_4		14.4		-11.9

[a] Energies are given in kcal/mol. Bond lengths are given in angstroms. The phenyl groups on the boron centers and the hydrogen atoms attached to carbons are omitted for clarity.

SiH_4 is found to be reversible as the reverse barrier is 26.3 kcal/mol (Table 2, entry 5).

FLP-catalyzed metal-free hydrogenation and hydroamination have been well studied in the past years.[2] However, the FLP-catalyzed hydrophosphination, a more challenging topic, has never been tackled. This might be a result of the strong coordination ability of the phosphine reactants, which could poison the catalyst. We were curious to simply model a complex involving a Me_2PH coordinated to either B1 or B4 of **1** but failed. The bond breaks up into **1** and free Me_2PH immediately during the optimization process, which is due to the high delocalization of the electrons stabilizing the electron-deficient boron centers and the aromaticity of the central ring. Thus, we presumed that **1** could catalyze the hydrophosphination of alkynes (Figure 4). In comparison, the direct hydrophosphination of phenylacetylene with Me_2PH was investigated computationally (see the Supporting Information for details), showing a high energy barrier (41.2 kcal/mol). Gratifyingly, from **IN2A**, three simple steps could be identified to complete the catalytic cycle, including the nucleophilic attack on C7 by Me_2PH, hydrophosphination, and catalyst recycling. The rate-determining step is computed to be the hydrophosphination step with the energy of 31.7 kcal/mol (**IN2A** → **TS5A**), and the catalytic cycle is highly exergonic by −31.3 kcal/mol to regenerate the active species **1**. Therefore, one can realize that the first boron−boron FLP **1** reported by the Kinjo group is a potentially useful catalyst in unsaturated organic substrate functionalizations.

■ CONCLUSION

The first intramolecular boron−boron FLP **1** was deeply analyzed by means of DFT calculations. The stability of **1** is due to the high delocalization of the electrons. The electronic effects and favorable orbital overlap of **1** with substrates plays a crucial role in the high regioselectivity of the ensuing products. The combination of aldehyde, ketone, imine, and silane with **1** are found to be reversible, especially at elevated temperatures. It seems that **1** can catalyze the hydrophosphination of Me_2PH and phenylacetylene due to the low activation barrier of 31.7 kcal/mol for the rate-determining step. These results suggest that **1** could be a powerful organocatalyst in the functionalizations of unsaturated substrates, such as hydrogenation, hydroamination, hydroborylation, hydrophosphination, and hydrosilylation. Our

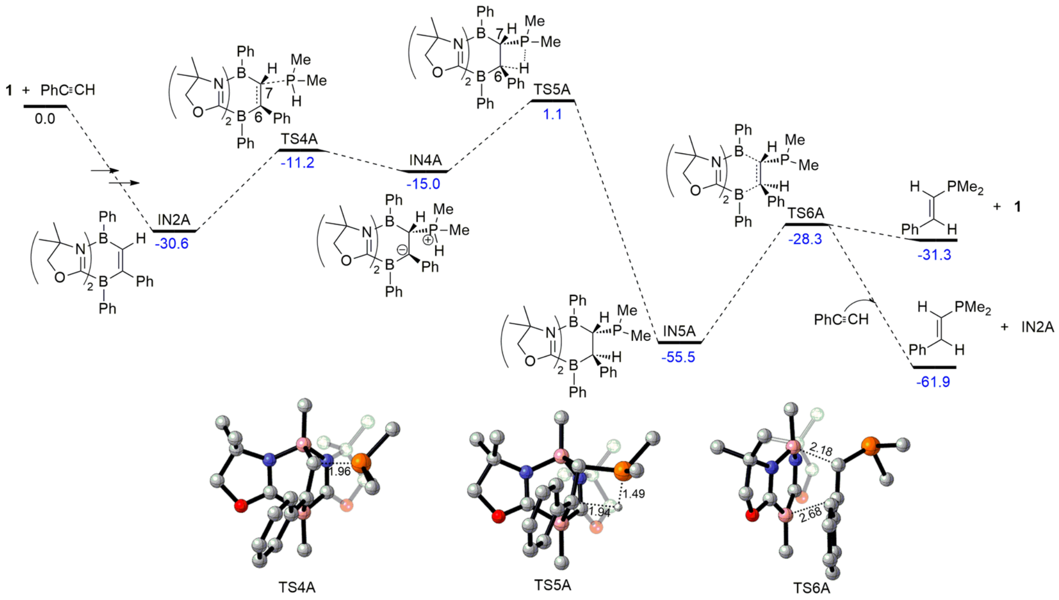


Figure 4. Hydrophosphination of phenylacetylene catalyzed by **1**. Energies are given in kcal/mol. Bond lengths are given in angstroms. The phenyl groups on the boron centers and the hydrogen atoms attached to carbons are omitted for clarity.

results may open a new avenue on design of novel organocatalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01726.

> Calculated energies, energy profile of catalyst-free hydrophosphination, strong interactions between the HOMOs of **1** and the LUMOs of substrates, Cartesian coordinates for all the species (PDF)

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Notes

The authors declare no competing financial interest.

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